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The role of oxygen in anaerobic microbiologically influenced marine corrosion

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ABSTRACT

The relationship between oxygen and microbiologically influenced corrosion (MIC) resulting from obligate anaerobic microbial processes is complex. Most reported cases of MIC of carbon steel and copper alloys in marine environments are caused by sulphate-reducing bacteria (SRB) with some dissolved oxygen in the bulk medium. Yet most laboratory experiments with SRB are conducted in the absolute absence of oxygen. The presence of oxygen can determine the rate and extent of corrosion resulting from obligate anaerobic microbial processes. Furthermore, the concentration of oxygen and the manner in which it is removed can affect experimental results. The specific coupled reactions for which oxygen is the final electron acceptor can vary. The role of oxygen in anaerobic MIC in both field and laboratory studies will be reviewed with an emphasis on SRB.

KEY WORDS

sulphate-reducing bacteria, oxygen, copper, carbon steel

INTRODUCTION

Sulphate-reducing bacteria (SRB) are the organisms most closely identified with microbiologically influenced corrosion (MIC). They are a group of ubiquitous, diverse anaerobes that use sulphate as the terminal electron acceptor, producing hydrogen sulphide. SRB have been the focus of many investigations involving MIC and several corrosion mechanisms have been attributed to SRB, including cathodic depolarization by the enzyme dehydrogenase, anodic depolarization, production of corrosive iron sulphides, release of exopolymers capable of binding metal ions, sulphide-induced stress corrosion cracking and hydrogen induced cracking or blistering. SRB have been isolated from a variety of environments^{1,2} including seawater where the concentration of sulphate is typically 25 mM.² Even though the oxygen content of seawater above the thermocline ranges from 5-8 part-per-million (ppm), anaerobic microorganisms survive in anaerobic microniches until conditions are suitable for their growth.^{3,4}

Hamilton *et al.*⁵ demonstrated that SRB can grow in communities or consortia within biofilms between 25 μm and 100 μm thick. If the aerobic respiration rate within a biofilm is greater than the oxygen diffusion rate, the metal/biofilm interface can become anaerobic and provide a niche for sulphide production by SRB. The critical biofilm thickness required to produce anaerobic conditions depends on availability of oxygen and the respiration rates of organisms in the biofilm. The metabolic activity of SRB causes accumulation of sulphide near metal surfaces and corrosion of vulnerable metals and alloys, including carbon steel and copper.

Relationship Between SRB-induced Corrosion and Oxygen

Syrett⁶ indicated that aggressive sulphide-induced corrosion of copper alloys required turbulence or oxygen, in addition to sulphides. The general phenomenology of SRB-MIC of copper alloys can be summarized as follows. Microbial consortia that include SRB produce anoxic, sulphide-rich environments in which the conversion of copper to copper sulphides is thermodynamically favored at a concentration of 10^{-2} M total sulphur. The first sulphur-poor compounds are converted to sulphur-rich compounds. It has been argued that if the copper sulphide layer were djurelite ($C_{1.96}S$), the sulphide layer would be protective.⁷ Even if such a sulphide film were technically passivating, the mechanical stability of the film is so poor that sulphide films are useless for corrosion protection. In the presence of turbulence, the loosely adherent sulphide film is removed, exposing a fresh copper surface to react with sulphides. For these reasons, turbulence-induced corrosion and sulphide attack of copper alloys cannot easily be decoupled. In the presence of oxygen, the possible corrosion reactions in a copper sulphide system are extremely complex because of the large number of stable copper sulphides,⁸ their differing electrical conductivities, and catalytic effects. Transformations between sulphides or sulphides to oxides result in changes in volume that weaken the attached scale and oxide subscale, leading to spalling. Bared areas repassivate forming cuprous oxide.

Similarly, Hardy and Bown⁹ demonstrated the extreme corrosivity of biogenic sulphide films to mild steel exposed to the atmosphere. They used successive aeration-deaeration cycles to produce pitting. The highest corrosion rates in their experiments were observed during periods of aeration. They reported, "The similarity between the form of corrosion attack seen in these tests and the pitting corrosion often attributed to the SRB in the field, strongly suggests that exposing biogenic sulphide films on steel to air might account for their corrosivity." They did not establish the minimum quantity of air needed to initiate the pitting they observed.

Lee *et al.*^{10,11} designed field experiments to evaluate deoxygenation of natural seawater as a corrosion control measure for unprotected carbon steel seawater ballast tanks. Carbon steel exposed to cycles of deoxygenated seawater (<0.2 ppm O_2) and oxygenated atmosphere had higher corrosion rates than coupons exposed to either consistently aerobic or hypoxic conditions (Figure 1). They also demonstrated the difficulty of maintaining hypoxic seawater. Using a gas mixture it was possible to displace dissolved oxygen. However, aerobic respiration and corrosion reactions consumed oxygen and produced absolute anaerobic conditions within the first days of hypoxia. Under anaerobic conditions sulphide corrosion products formed. When gaskets and seals failed, oxygen was inadvertently introduced. The impact of oxygen ingress on corrosion depended on the amount of oxygen in the system at the time oxygen was introduced (Figure 1).

Hamilton¹² reviewed the data of others and proposed a model for MIC in which he concluded that all mechanisms, both aerobic and anaerobic, involved a process of electron transfers from base metal to oxygen as the ultimate electron acceptor through a series of coupled reactions (Figure 2). He proposed that in the case of SRB and carbon steel, sulphate, an intermediate electron acceptor, is reduced to sulphide that reacts with iron to form a corrosion product that ultimately transfers electrons to oxygen. In the model, sulphate is the terminal electron acceptor in anaerobic respiration, but oxygen is the terminal electron acceptor in the corrosion reaction. In his model, he hypothesized that "microbial action has supplied products which are thermodynamically compatible with the potentials of the putative corrosion reactions of the relevant substratum and critically, has generated appropriate kinetically favoured pathways of electron flow from the metal anode to the universal electron acceptor, oxygen." The examples presented in this paper support the Hamilton model.

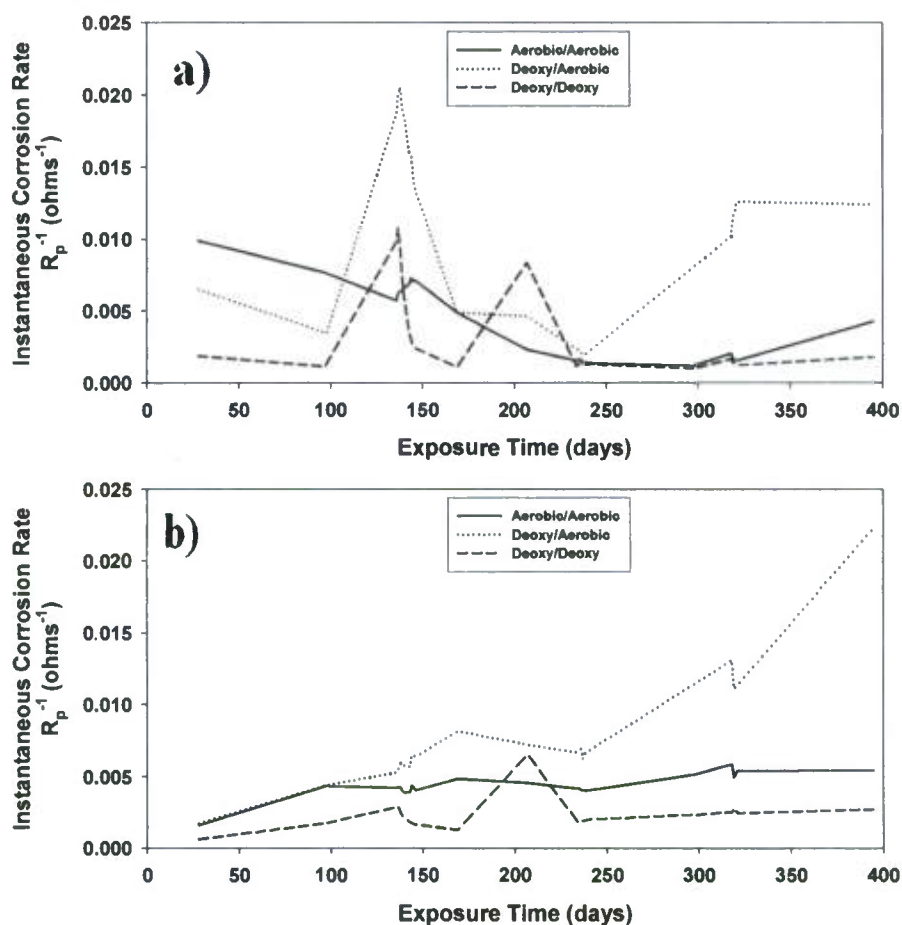


FIGURE 1. Carbon steel 1020 (CS) instantaneous corrosion rate ($1/R_p$ ohms^{-1}) in natural seawater as a function of oxygen concentration in the water/headspace. a) Vertically orientated CS coupons in the middle of the water column. b) Upward-facing horizontally orientated CS coupons at the bottom of the water column. Aerobic = open-to-air; Deoxy = $[\text{O}_2]$ less than 0.2 parts-per-million.

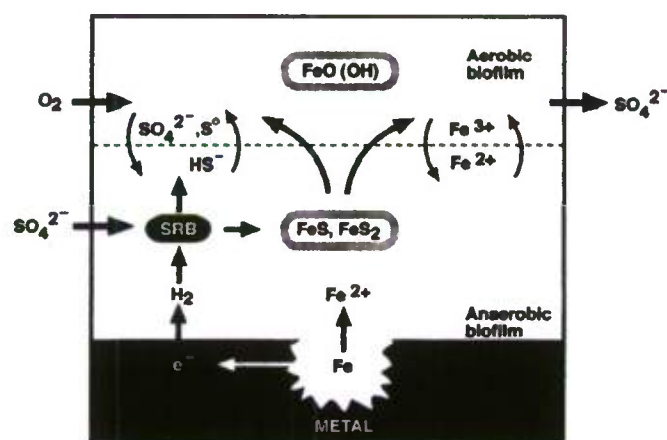
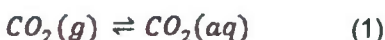


Figure 2. A descriptive model of the corrosion of mild steel resulting from the action of sulphate-reducing bacteria in a mixed aerobic/anaerobic system in which oxygen acts as the terminal electron acceptor.¹² (Reproduced with the permission of Hamilton, *Biofouling* 2003)

Laboratory Methods for Removing Oxygen

Many laboratory experiments with SRB rely on gas purging to remove oxygen and create an anaerobic environment in the laboratory solution of choice i.e., natural/artificial seawater or culture media. The pH of carbonate-buffered synthetic and natural seawater is controlled (buffered) by carbon dioxide (CO₂). Gaseous carbon dioxide {CO₂(g)} from the atmosphere dissolves into seawater forming aqueous carbon dioxide {CO₂(aq)} (1), reacts with water, and forms carbonic acid (H₂CO₃) (2). Proton dissociation from H₂CO₃ proceeds with interdependence on pH. The first proton dissociation forms bicarbonate (HCO₃⁻) (3), with carbonate (CO₃²⁻) formation from subsequent proton dissociation (4).



Increasing atmospheric [CO₂(g)] increases dissolved [CO₂(aq)], which elevates [H₂CO₃] resulting in decreased seawater pH. If CO₂(aq) is removed from seawater, pH increases.

Lee *et al.*¹³ evaluated the influence of deoxygenation techniques on seawater microbiology and chemistry. They maintained two coastal seawaters (Key West, FL, USA [KW] and Mina Sulman, Bahrain [PG]) under two laboratory conditions: 1) deoxygenation with bubbled nitrogen gas (N₂) and 2) deoxygenation in an anaerobic hood. The anaerobic atmosphere was maintained using a gas mixture of 10% H₂, 5% CO₂, and 85% N₂. Hydrogen was added to the anaerobic gas mixture to aid in removal of O₂. A palladium catalyst inside the anaerobic chamber served as an O₂ and H₂ reaction site resulting in the formation of water and increased humidity. Humidity was maintained between 20 – 30% using an alumina desiccant. Atmospheric O₂ concentration was continuously monitored at less than one ppm. In parallel experiments house N₂ was bubbled into the seawaters. Bubbling was not vigorous with approximately two bubbles-per-second. No nutrients or other additions were made to any of the exposure conditions. In all experiments, pH, dissolved sulphide and planktonic microbial populations were monitored.

Exposure to the mixed gas anaerobic environment caused decreased pH values in both seawaters to below 7.0. Bubbling N₂ had the opposite effect, causing an increase in pH to above 9.0. Anaerobic stagnant seawaters maintained in an anaerobic hood with mixed gases produced over 10¹ to 10³ part-per-billion (ppb) dissolved sulphide. Seawaters maintained with bubbled N₂ produced over 10¹ ppb dissolved sulphide during the course of the experiment, but below detection limits at the conclusion of the experiment (Figure 3). The planktonic microbial population that one was able to detect was determined by the way the water was maintained. The microbial populations were followed using liquid culture techniques that are recognized as capable of growing only a small percentage of the natural populations. Liquid culture techniques can be used to make comparisons, but not to make determinations about population diversity. Generally, KW seawater had higher bacterial numbers in all exposure conditions when compared to PG seawater. Bubbling N₂ through the seawaters produced the lowest concentration of bacteria in comparison to seawater left open to air and that tested in the anaerobic chamber.

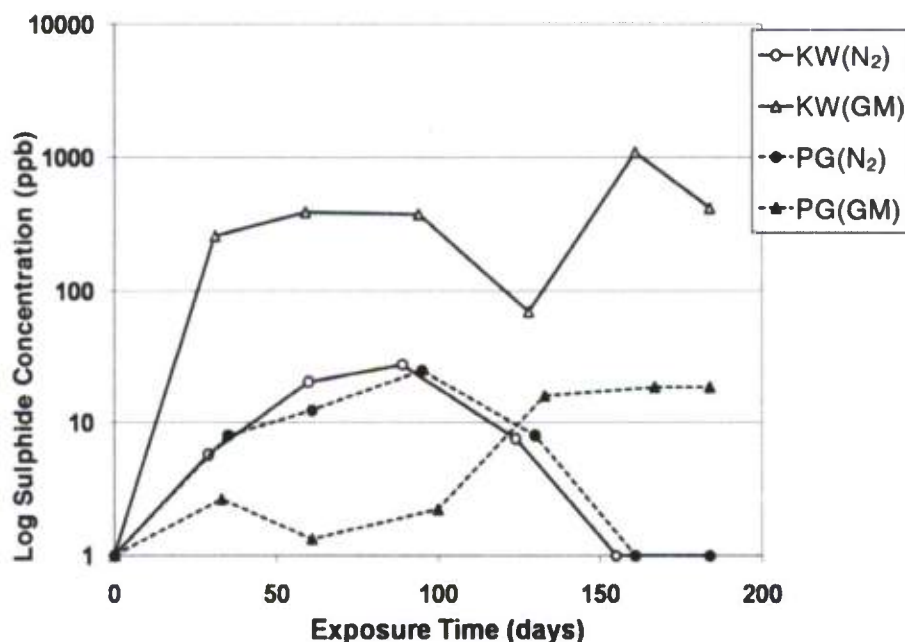


FIGURE 3. Log sulphide concentration in parts per billion (ppb) as a function of exposure time (days) for Key West seawater (KW) and Persian Gulf seawater (PG) under nitrogen bubbled (N₂) and gas mixture (GM) conditions. Seawaters exposed to air exhibited sulphide levels below detection limits.

Aktas *et al.*¹⁴ recently demonstrated another important consequence of using gas mixtures to remove oxygen. In a series of experiments that were meant to duplicate each other, researchers at the University of Oklahoma (OU), Norman, OK, USA, and the Naval Research Laboratory (NRL), Stennis Space Center, MS, USA, biodegradation of petroleum and biofuels was evaluated in the presence of natural seawater from Key West, FL. Both laboratories used the same starting materials, i.e., the same fuels and the same seawaters. However, in the NRL experiment, the systems were allowed to achieve anaerobic conditions naturally as a result of aerobic respiration and corrosion reactions. In the OU experiments dissolved oxygen was replaced with a headspace gas N₂/CO₂ (8:2). Sulphate removal was monitored (Figure 4). At the end of three months sulphate was depleted from the NRL experiments and fuel degradation products were indicative of aerobic pathways. When oxygen was removed from tanks using an anaerobic gas mixture fuel degradation products were consistent with anaerobic pathways. Corrosion under the two circumstances is being investigated.

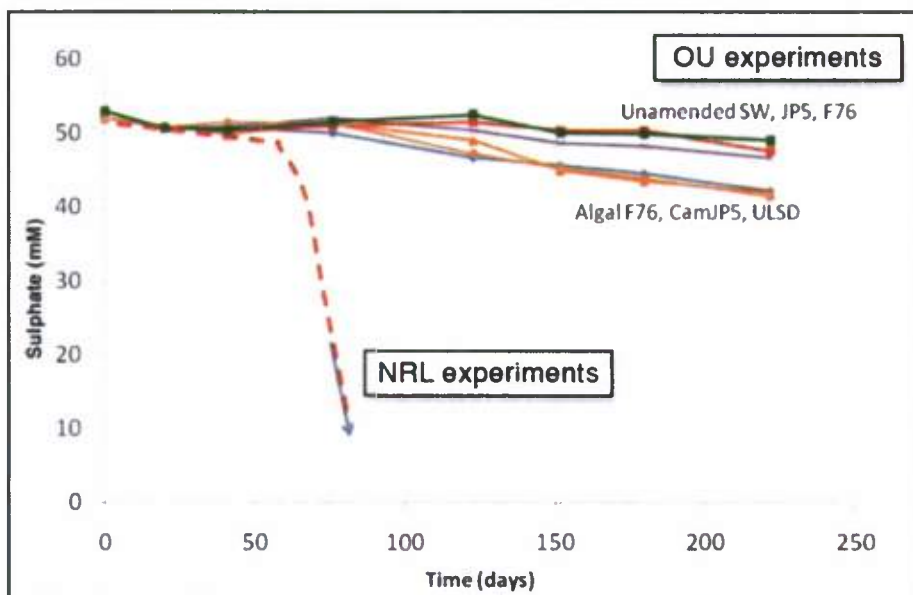


Figure 4. Sulphate removal during anaerobic biodegradation of fuels. SW – seawater, JP5 – jet petroleum, F76 – petroleum diesel, algal F76 – Algal derived diesel, Cam/JP5 – camelina-derived jet fuel, USLD – ultra low sulphur diesel.

CONCLUSIONS

Data reviewed in this paper emphasize the importance of dissolved oxygen and the techniques for removing oxygen on the outcome of laboratory experiments involving SRB. Laboratory experiments that mimic anaerobic conditions by bubbling pure nitrogen gas may not produce conditions found in natural seawater due to pH changes. The effect of oxygen must also be considered when interpreting field data.

ACKNOWLEDGEMENTS

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